

Materials Science and Technology Nanoscience

Small Particles for Solving Big Problems: Using MOFs for Nanoparticle Synthesis

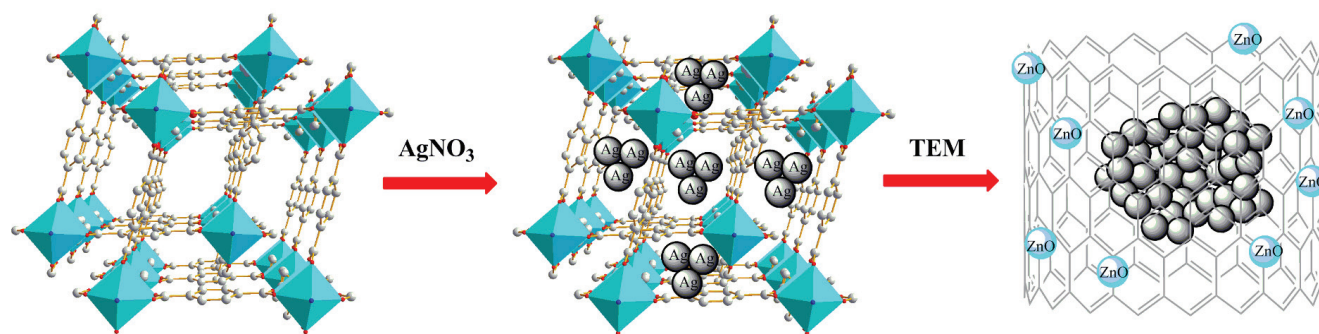


Figure 1: Using MOFs to create nanoclusters. *Left:* empty MOF structure (blue: octahedrally-coordinated zinc atoms; red: oxygen; blue: nitrogen; gray: carbon); *Middle:* silver-infiltrated MOF following *in-situ* reduction to create nanoclusters stabilized by the framework. *Right:* subsequent exposure to a high energy TEM beam breaks down the MOF and allows Ag agglomeration.

Versatile nanoporous materials allow new approaches to both nanoparticle synthesis and hydrogen storage

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Shrinking materials to nanoscale dimensions can have interesting and potentially useful consequences. For example, gold particles in the 10–100 nm size range can emit bright light and be used to track individual molecules in biological systems. Even smaller particles are being investigated for their potential as “super catalysts.” On a commercial scale, silver nanoparticles have been incorporated into washing machines because of their antibacterial properties. However, both the synthesis and the characterization of nanomaterials present major scientific and engineering challenges, particularly when their dimensions are smaller than 10 nm.

Sandia is developing novel nanoporous materials known as metal-organic frameworks (MOFs) as templates for nanoparticles. A typical MOF (Figure 1) consists of positively-charged metal atoms such as Zn^{+2} linked by negatively-charged organic groups such as carboxylates (CO_2^-), yielding a rigid, open framework that can accommodate guest atoms and molecules. The pore size and chemical properties

of MOFs can be tailored for applications ranging from gas storage to sensing. The interior dimensions of MOF pores range from less than 1 nm to about 5 nm and have enclosed pores or one-dimensional open channels. Two examples are given here that demonstrate the extremely versatile MOF platform for both probing unusual effects in nanoscale particles, and to also serve as a novel synthetic tool for creating particles of controlled size and shape.

The first example concerns the creation of silver nanoparticles within MOF templates (see Figure 1). MOF pores infiltrated with solutions of silver nitrate and ethanol generate nanoparticles because ethanol reduces the Ag^{+1} ions to uncharged silver (Ag^0), creating silver particles so small they cannot be seen even by transmission electron microscopy (TEM). The smallest particles have only three atoms (Ag_3) and can be clearly identified by their magnetic properties; the largest particles have approximately 20 atoms, which are about 0.7 nm in diameter. The particles are stabilized by oxygen-containing groups

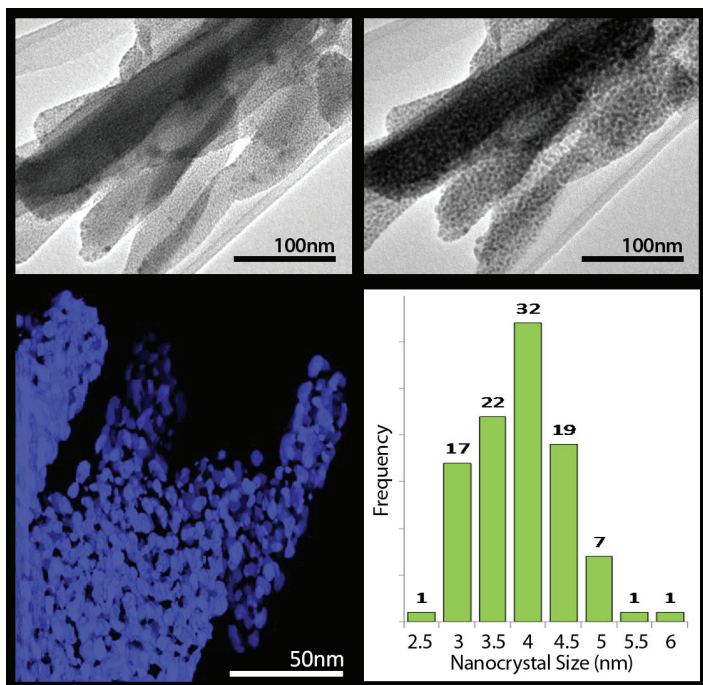


Figure 2: Before and after images of Ag@MOF. *Top left:* Image of Ag@MOF before significant electron beam damage. *Top right:* Image of Ag@MOF after 1 minute electron beam exposure, showing formation of larger silver particles (small black dots). *Bottom left:* tomographic image showing silver nanoparticles throughout a MOF crystal. *Bottom right:* size distribution of TEM-synthesized Ag nanoparticles, where the average size is 3.9 ± 0.65 nm.

within the MOF structure that also prevent particle diffusion through the pore openings of the template. However, they are still accessible to solvent and other small molecules, thus creating a platform for probing their chemistry. Larger particles ranging in size from just a few nanometers to tens of nanometers can be formed by decomposing the template with the TEM electron beam or by heating the sample to 250–310 °C (Figure 1 right, and Figure 2). As shown in Figure 2, the size distribution can be quite narrow. Also, the electron beam synthetic method has been generalized to create nanoparticles from the MOF templates alone, with success in making bare copper and indium nanoparticles, as well as zinc oxide nanoparticles. These results demonstrate the versatility of the “metal@MOF” platform, which has significant advantages for nanoparticle synthesis. For example, MOF templates avoid the use of bulky capping molecules needed to prevent agglomeration in solution-based nanoparticle synthesis (the capping molecules can inhibit nanoparticle utility).

The second example concerns the use of MOF templates to create nanoparticles of metal hydrides for hydrogen storage. Recent theory and experiment suggest that shrinking metal hydrides to the nanoscale enables tuning of hydrogen

desorption thermodynamics and kinetics, potentially allowing hydrides that are normally irreversible in the bulk phase to be used for vehicular hydrogen storage. Sandia is systematically probing the effects of size and pore environment on metal hydride H_2 desorption kinetics using MOF templates, which are an attractive alternative to materials such as aerogels and mesoporous silica that have a distribution of pore sizes. Experiments show that MOFs are stable hosts for several metal hydrides and that nanoclusters on the scale of MOF pores can be synthesized. These materials exhibit reduced H_2 desorption temperatures and accelerated desorption kinetics (Figure 3). The results provide a scientific basis for designing nanoscale hydrides with desorption rates appropriate for hydrogen storage applications.

These examples illustrate the versatility of MOFs to serve as templates for a wide variety of nanoparticles and to probe their properties. Sandia’s research is now aimed at a better understanding of the underlying mechanisms for particle formation, growth, and stabilization, so that they can be employed in practical applications.

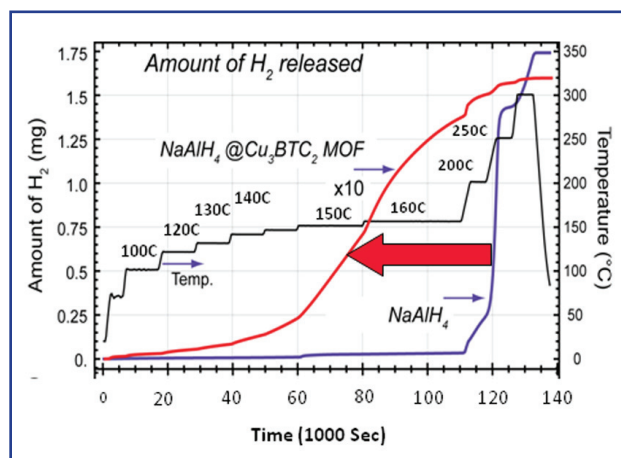


Figure 3: Amount of H_2 released from MOF infiltrated with $NaAlH_4$ (red line) compared with bulk-phase $NaAlH_4$ (blue line). The stepped black line in the plot indicates the temperature profile used to heat the samples.

References:

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